Ab initio Study of Valley Line on a Total-Energy Surface for Zone-Center Distortions of Ferroelectric Perovskite Oxides BaTiO₃ and PbTiO₃

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(Dated: February 2, 2008)

An *ab initio* structure optimization technique is newly developed to determine the valley line on a total-energy surface for zone-center distortions of ferroelectric perovskite oxides and is applied to barium titanate (BaTiO₃) and lead titanate (PbTiO₃). The proposed technique is an improvement over King-Smith and Vanderbilt's scheme [Phys. Rev. B **49**, 5828 (1994)] of evaluating total energy as a function of the amplitude of atomic displacements. The results of numerical calculations show that total energy can be expressed as a fourth-order function of the amplitude of atomic displacements in BaTiO₃ but not in PbTiO₃.

The ABO_3 perovskite oxides, such as barium titanate (BaTiO₃) and lead titanate (PbTiO₃), are extremely important ferroelectric materials. Because of their piezoelectricity below Curie temperatures (408 and 763 K, respectively [1]) and large dielectric constants, they are widely used in various applications and they have been extensively studied experimentally and theoretically. At room temperature, BaTiO₃ and PbTiO₃ have tetragonal (C_{4v}^1) structures and spontaneous polarization. The tetragonal structure can be understood to be a result of displacive transitions from their high-temperature cubic (O_h^1) structures, as depicted in Fig. 1. The spontaneous polarization is a result of the displacements of cations A and B and three O²⁻'s to the opposite directions. While these two classic examples of ferroelectric perovskite oxides, BaTiO₃ and PbTiO₃, have similar properties, such as crystal structure and unit-cell volume (64.4 and 63.4 Å³, respectively), they have significantly different structural parameters and properties, such as the ratio of lattice constants c/a (1.01 and 1.06, respectively), atomic displacements (in BaTiO₃ the atomic displacement of B =Ti is larger than that of A =Ba, but in PbTiO₃ that of A=Pb is larger than that of B=Ti), dielectric constants, and piezoelectric constants. Cohen

used the all-electron, full-potential, linearized augmented plane-wave (FLAPW) method to study the atomic and electronic structures of BaTiO₃ and PbTiO₃ [2]. He pointed out that the hybridization between Ti 3d and O 2p is strong and essential to weaken the short-range repulsions and allow the ferroelectric transition in both BaTiO₃ and PbTiO₃. He also pointed out that the hybridization between Pb 6s and O 2p is strong so that it modifies the ground state and nature of the transition of PbTiO₃ by (1) increasing the ferroelastic strain that couples with the ferroelectric distortions or (2) hybridizing with the valence states, leading indirectly to changes in the Ti-O interactions, whereas the interaction between Ba and O is almost ionic in tetragonal BaTiO₃. Recently, using synchrotron orbital radiation high-energy X-rays, Kuroiwa *et al.* confirmed the covalent bonding between Pb-O and the ionic bonding between Ba-O [3].

To investigate ferroelectric perovskite oxides, it is useful to estimate the total-energy surface for zone-center distortions accurately under absolute zero temperature by *ab initio* calculations. King-Smith and Vanderbilt studied the total-energy surface using ultrasoft-pseudopotentials and a plane-wave basis set [4]. From the full symmetric cubic perovskite structure, they gave the displacements v_α^τ of atoms τ (=A, B, O₁, O₂, O₃) in the Cartesian directions of α (= x, y, z) along the Γ_{15} soft-mode normalized eigenvectors $\boldsymbol{\xi}_\alpha$ as

$$\mathbf{v}_\alpha = \begin{pmatrix} v_\alpha^A \\ v_\alpha^B \\ v_\alpha^{O_1} \\ v_\alpha^{O_2} \\ v_\alpha^{O_3} \end{pmatrix} = u_\alpha \boldsymbol{\xi}_\alpha = u_\alpha \begin{pmatrix} \xi_\alpha^A \\ \xi_\alpha^B \\ \xi_\alpha^{O_1} \\ \xi_\alpha^{O_2} \\ \xi_\alpha^{O_3} \end{pmatrix}, \qquad (1)$$

with the scalar soft-mode amplitude u_α. Under the condition that the strain components η_i ($i = 1, \ldots, 6$; Voigt notation) minimize the total energy for each u_α, they expressed the total-energy surface as

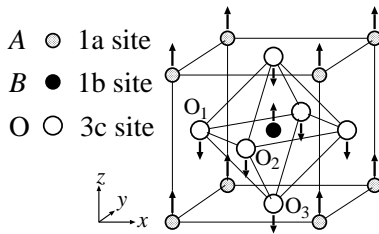$$E_{\text{tot}} = E^0 + \kappa u^2 + \alpha' u^4 + \gamma'(u_x^2 u_y^2 + u_y^2 u_z^2 + u_z^2 u_x^2), \quad (2)$$

FIG. 1: Cubic crystal structure of perovskite oxide ABO_3. The cubic-tetragonal displacive transition accompanies atomic displacements v_z^τ (τ=A, B, O₁, O₂, O₃) indicated by arrows.
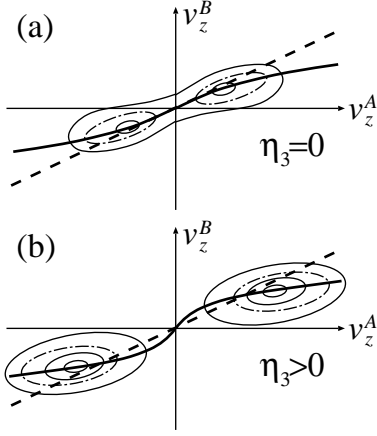
A ○ 1a site
B ● 1b site
O ○ 3c site

FIG. 2: The total-energy surface for zone-center distortions of ferroelectric perovskite oxides are schematically illustrated with contour lines for two strains (a) $\eta_3 = 0$ and (b) $\eta_3 > 0$ in the two-dimensional subspace (v_z^A, v_z^B) of the atomic-displacement space $(v_z^A, v_z^B, v_z^{O_1}, v_z^{O_2}, v_z^{O_3})$. Thick solid lines are the valley lines for fixed η_3's. Dashed lines show the *direction* of the Γ_{15} soft-mode eigenvector at zero strain. Note that the *direction* is tangential to the valley line at $v_z^\tau = 0$ for $\eta_3 = 0$, but this is not the case for $\eta_3 \neq 0$.

where $u^2 = u_x^2 + u_y^2 + u_z^2$, E^0 is the total energy for the cubic structure, κ is one-half of the eigenvalue of the soft mode, and α' and γ' are the constants determined from coupling constants between atomic displacements and strains. Although their expression veritably describes essential properties of atomic displacements coupling with strains, it may misestimate (a) the energy gain of the lattice distortion from the cubic structure to the tetragonal equilibrium structure due to a deviation of atomic displacements from the soft-mode $\boldsymbol{\xi}_\alpha$ *direction* as illustrated in Fig. 2, as well as (b) the total energy particularly when the amplitude of atomic displacements u_z is larger than the equilibrium value. Also, (c) α' and γ' in eq. (2) strongly depend on coupling constants between atomic displacements and strains, but the coupling constants, $B_{1xx} = \partial^3 E / \partial\eta_1 \partial u_x^2$ for instance, are *not* always constant through out all the way from the cubic structure to the distorted equilibrium structure, and thus they are difficult to determine. These issues, (a)-(c), arise because King-Smith and Vanderbilt's expression is restricted within the atomic displacements corresponding to the Γ_{15} soft-mode eigenvector at zero strain and also within the fourth-order function of u_α, as in eq. (2). In this work, therefore, we redefine the amplitude of atomic displacements as

$$u_\alpha = \sqrt{\left(v_\alpha^A\right)^2 + \left(v_\alpha^B\right)^2 + \left(v_\alpha^{O_1}\right)^2 + \left(v_\alpha^{O_2}\right)^2 + \left(v_\alpha^{O_3}\right)^2}, \quad (3)$$

and evaluate the total energy as a function of u_α under the condition that v_α^τ and η_i minimize the total energy for each u_α using an *ab initio* norm-conserving pseudopo-

tential method and geometric optimization. Note that the translational displacement should be omitted both in eq. (1) and in eq. (3), i.e., the condition that

$$v_\alpha^A + v_\alpha^B + v_\alpha^{O_1} + v_\alpha^{O_2} + v_\alpha^{O_3} = 0 \quad (4)$$

should be satisfied. Although, below room temperature, BaTiO$_3$ exhibits tetragonal–orthorhombic (C_{2v}^{14})–rhombohedral (C_{3v}^5) structure transitions and the total energy can be defined as a function of u_x, u_y, and u_z, we restrict our argument, in this paper, only to the cubic–tetragonal distortion; $E_{\text{tot}} \equiv E_{\text{tot}}(u_x = 0, u_y = 0, u_z)$ and we optimize the strains $\eta_1 = \eta_2$ and η_3 while η_4, η_5, and η_6 are kept at zero.

Minimization of total energy under the constant-u_α constraint, i.e., on the constant-u_α sphere, is carried out iteratively. Suppose that at the previous iteration indexed k we calculated a gradient $\mathbf{g}$, i.e., forces exerted on atoms, and a symmetric Hessian matrix B, i.e., the second derivative of total energy $B_{\sigma\tau} = d^2 E_{\text{tot}}/dv_z^\sigma dv_z^\tau$, at displacement vector $\mathbf{v}_{z,k}$. In the neighborhood of $\mathbf{v}_{z,k}$, total energy has the form

$$E_{\text{tot}}(\mathbf{v}_z) = \frac{1}{2}{}^t(\mathbf{v}_z - \mathbf{v}_{z,k})B(\mathbf{v}_z - \mathbf{v}_{z,k})$$
$$+ {}^t(\mathbf{v}_z - \mathbf{v}_{z,k})\mathbf{g} + E_{\text{tot}}(\mathbf{v}_{z,k}), \quad (5)$$

where t's indicate the transpose of vectors. We first minimize eq. (5) on a plane that includes $\mathbf{v}_{z,k}$ and is perpendicular to $\mathbf{n} = \mathbf{v}_{z,k}/|\mathbf{v}_{z,k}|$, i.e., on a plane that touches the constant-u_α sphere at $\mathbf{v}_{z,k}$. This constraint can be expressed as

$${}^t(\mathbf{v}_z - \mathbf{v}_{z,k})\mathbf{n} = 0. \quad (6)$$

The method of Lagrange multipliers specifies that the gradients of eq. (5) and eq. (6) must be proportional. Thus, a trial displacement $\mathbf{v}'_{z,k+1}$ for the next iteration $k+1$ can be determined by solving

$$B(\mathbf{v}_z - \mathbf{v}_{z,k}) + \mathbf{g} = \lambda\mathbf{n}, \quad (7)$$

where λ is a Lagrange multiplier. We can determine the Lagrange multiplier $\lambda = {}^t\mathbf{n}B^{-1}\mathbf{g}/{}^t\mathbf{n}B^{-1}\mathbf{n}$, and now we obtain

$$\mathbf{v}'_{z,k+1} = \mathbf{v}_{z,k} - B^{-1}(\mathbf{g} - \frac{{}^t\mathbf{n}B^{-1}\mathbf{g}}{{}^t\mathbf{n}B^{-1}\mathbf{n}}\mathbf{n}), \quad (8)$$

but $|\mathbf{v}'_{z,k+1}|$ may be slightly different from u_z. Hence, we use

$$\mathbf{v}_{z,k+1} = \frac{\mathbf{v}'_{z,k+1}}{|\mathbf{v}'_{z,k+1}|}u_z \quad (9)$$

as a trial displacement for the next iteration. The strains $\eta_1 = \eta_2$ and η_3, i.e., lattice constants a and c, are optimized simultaneously in the iterations. We continue

this iterative scheme of optimizing the atomic and lattice structure until the differences in total energies become less than 10^{-7} Hartree twice successively.

In the case of chemical reactions of molecules, a reaction path can be defined as the steepest-descent path from a transition structure down to reactants and down to products, i.e., the valley line [5]. Although there are some techniques to determine the chemical reaction path [6], we expect our optimization technique to be accurate enough and to give a simple approximation for the ABO_3 perovskite oxides.

We use the ABINIT package [7] for all *ab initio* calculations. Bloch wave functions of electrons are expanded into plane waves with a cut-off energy of 60 Hartree, using Teter's extended norm-conserving pseudopotentials [8]. The pseudopotentials include O 2s and 2p, Ti 3s, 3p, 3d and 4s, Ba 5s, 5p and 6s, and Pb 5d, 6s and 6p as valence electrons. Bloch wave functions are sampled on an $8 \times 8 \times 8$ grid of k-points in the first Brillouin zone. The grid is reduced to 40 irreducible k-points under C_{4v}^1 symmetry. The exchange-correlation energy is treated within the local density approximation (LDA). As the parametrized correlation energy, we use Teter's rational polynomial parametrization [9], which reproduces the results obtained by Ceperley and Alder [10]. The electronic states are calculated by the iterative scheme to reach a tolerance of convergence that requires differences of forces to be less than 5×10^{-7} Hartree/Bohr twice successively.

The presently calculated ratios of lattice constants c/a and the amplitudes of atomic displacements u_z for the tetragonal equilibrium structures are $c/a = 1.0029$ and $u_{z,\mathrm{eq}} = 0.0975$ Bohr for BaTiO$_3$ and $c/a = 1.0284$ and $u_{z,\mathrm{eq}} = 0.6087$ Bohr for PbTiO$_3$. The experimentally observed values are $c/a = 1.0086$ and $u_{z,\mathrm{eq}} = 0.2638$ Bohr for BaTiO$_3$ [11] and $c/a = 1.0649$ and $u_{z,\mathrm{eq}} = 0.9076$ Bohr for PbTiO$_3$ [3]. Thus, calculations underestimate the experimental values. Calculated energies gained through cubic to tetragonal distortions are 0.386 meV in BaTiO$_3$ and 37.5 meV in PbTiO$_3$. Although energy gain and experimentally observed transition temperature (408 K = 35.2 meV for BaTiO$_3$ and 763 K = 65.8 meV for PbTiO$_3$) cannot be compared directly, the energy gains also seem to be underestimated. These underestimations are because the large sensitivity to volume makes the volume errors in LDA unusually important [2]. Nevertheless, we believe that calculations using LDA clarify some trends of displacive transitions of perovskite oxides.

Figure 3 shows the obtained results for BaTiO$_3$. We can see that total energy is well expressed as a fourth-order function of the amplitude of atomic displacements u_z (Fig. 3(a)). Lattice constants a and c are also well fitted with the quadratic function of u_z (Fig. 3(b)). These results suggest that for the compound with the small spontaneous distortion the *direction* of atomic displacements remains almost equal to the soft-mode eigenvector
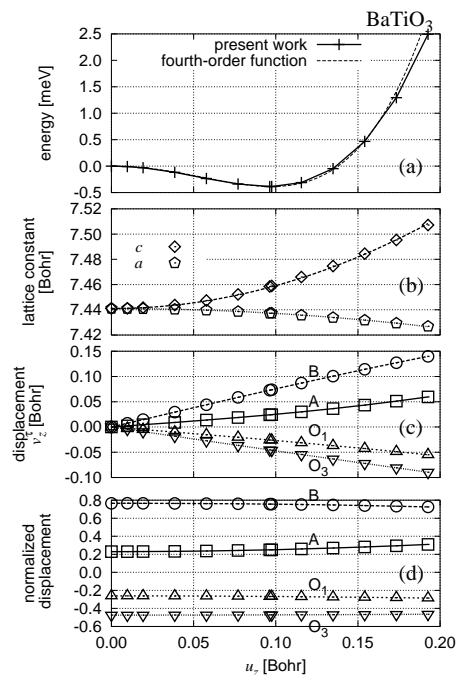

FIG. 3: (a) Calculated total energy in meV as a function of u_z in Bohr for BaTiO$_3$ (+'s connected with solid lines) compared with a fourth-order function that passes through the calculated energy minimum at $u_z = 0.0975$ Bohr and the maximum at $u_z = 0$ (dashed line). Zero of the energy scale is placed at the total energy of the cubic structure when $u_z = 0$. (b) Lattice constants a and c in Bohr as functions of u_z fitted by quadratic functions drawn with a dotted line and a dashed line, respectively. (c) Atomic displacements $v_z^A, v_z^B, v_z^{O_1} = v_z^{O_2}, v_z^{O_3}$ as functions of u_z. (d) Normalized atomic displacements v_z^τ / u_z as functions of u_z. The Γ_{15} soft-mode eigenvector $\boldsymbol{\xi}_z$ calculated by the frozen phonon method is additionally shown at $u_z = 0$.

$\boldsymbol{\xi}_z$ through out the speculating range of atomic displacements, as shown in Fig. 3(d), and thus the total energy can be well expressed within the fourth order expansion.

In PbTiO$_3$, on the contrary, total energy cannot be expressed as a fourth-order function of u_z, as shown in Fig. 4(a). We can see in Fig. 4(b) that lattice constant c is not well fitted by the quadratic function of u_z. These are due to the deviation of atomic displacements from the soft-mode $\boldsymbol{\xi}_\alpha$ *direction* as u_z becomes larger (Fig. 4(d)); from $u_z = 0$ to around $u_z = 0.6087$, at which the total energy becomes minimum, the normalized displacement of A=Pb increases and that of B=Ti decreases. Then, beyond $u_z = 0.6087$, that of O$_3$ decreases while that of O$_1$ slightly increases. This result is the first clarification of the non-fourth-order behavior of the total-energy surface, though it was predicted for the compounds with the largest spontaneous distortion [4], but has been difficult to formalize with coupling between atomic displacements and strains.
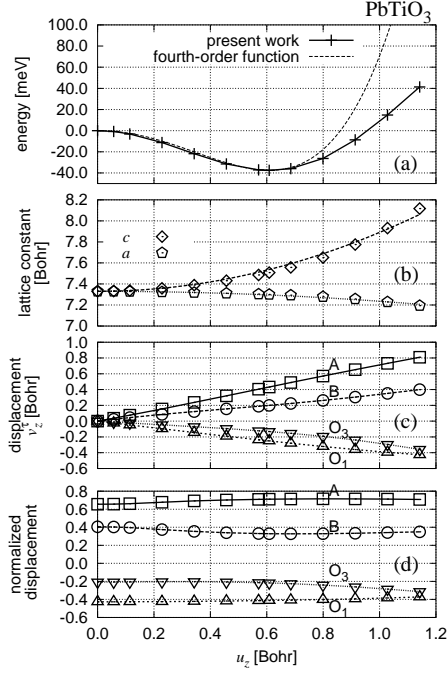
FIG. 4: (a)-(d) Same as Fig. 3 except the energy minimum is at $u_z = 0.6087$ for PbTiO$_3$. Note that scale of energy and displacements are larger than that in Fig. 3 and that the order of atomic displacements of PbTiO$_3$ in (c) and (d) is A, B, O$_3$, and O$_1$, from top to bottom, which is different from that of BaTiO$_3$.

The conventional Slater mode [12] $\boldsymbol{\xi}_{\text{Slater}} = {}^t(0\ 3\ -1\ -1\ -1)/\sqrt{12}$, is the dominant component of atomic displacements through out the entire speculating range in BaTiO$_3$, as it is well known. We find that it is useful to analyze normalized atomic displacements of PbTiO$_3$ with new three components, the A-O$_1$,O$_2$ closing mode $\boldsymbol{\xi}_{A-O_1,O_2} = {}^t(2\ 0\ -1\ -1\ 0)/\sqrt{6}$, the B-O$_3$ closing mode $\boldsymbol{\xi}_{B-O_3} = {}^t(0\ 1\ 0\ 0\ -1)/\sqrt{2}$, and the rest mode $\boldsymbol{\xi}_{\text{rest}} = {}^t(-2\ 3\ -2\ -2\ 3)/\sqrt{30}$. The dominant A-O$_1$,O$_2$ closing mode has its maximum at around $u_z = 0.6087$, at which the total energy becomes minimum, as shown in Fig 5. This can be understood as follows: from $u_z = 0$ to $u_z = 0.6087$ the covalent bonding between A-O$_1$,O$_2$ becomes stronger, but beyond $u_z = 0.6087$, rigid-sphere-like ionic repulsion between them becomes stronger. It is consistent with Cohen's description [2] and Kuroiwa *et al.*'s experimental work [3].

In summary, we contrived an *ab initio* structure optimization technique to determine the valley line on a total-energy surface for zone-center distortions of ferroelectric perovskite oxides and applied it to BaTiO$_3$ and PbTiO$_3$. (a) Our new optimization technique picks up the tetragonal equilibrium structure and gives its correct energy gain in principle. (b) The results of numerical calculations show that total energy can be expressed as a fourth-order function of the amplitude of atomic dis-
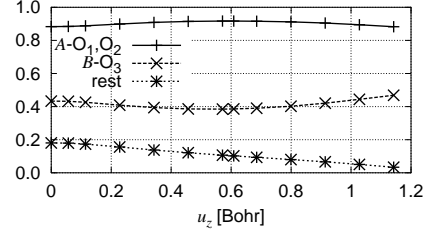

FIG. 5: Normalized atomic displacements of PbTiO$_3$ are decomposed into three modes: the A-O$_1$,O$_2$ closing mode (solid line), the B-O$_3$ closing mode (dashed line), and the rest mode (dotted line) as functions of u_z in Bohr.

placements u_z in BaTiO$_3$ but not in PbTiO$_3$. (c) Our new optimization technique can *automatically* evaluate the total energy as a function of u_z and coupling between atomic displacements and strains, i.e., the quadratic or nearly quadratic u_α-dependences of strains. This is an advantage of our technique compared with King-Smith and Vanderbilt's scheme.

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